

Electrostatic interactions in the presence of surface charge regulation: exact results

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Abstract – We study the problem of charge regulation and its effects on electrostatic interactions between dissociable charge groups immersed in a univalent electrolyte, within a family of one dimensional exactly solvable models. We consider the case of both charge regulated plates, but also the interaction of pairs of finite size dielectric "particles". Using the transfer matrix formalism we are able to determine the disjoining pressure as well as the correlations between the charge and the dipole moments of the objects as a function of their separation and electrolyte concentration.

Introduction. – The interaction of charged objects immersed in an electrolyte gives rise to a rich phenomenology which has been explored by a number of different methods [1]. In this paper we study one-dimensional models using a field theory formalism [2, 3] which was introduced by Edwards and Lenard [4], and adapted to surface properties and surface-surface interactions in [5, 6] and [7–9].

We are particularly interested in potential applications for the interactions between proteins [10], where it has been realised for a long time that fluctuations in surface amino acid charge dissociation state can give rise to a monopole-monopole fluctuation interaction as described by Kirkwood and Shumaker [11, 12]. Such a long-range fluctuation interaction is possible only for surfaces that exhibit charge regulation, that is, they do not have a fixed surface charge. When present these interactions decay, in three dimensions, as $1/r^2$ between point particles and vary consequently as $\log(D)$ between planar surfaces [7]. In the present paper we study effects of this type *exactly* in one dimension by using the surface dissociation model introduced by Ninham and Parsegian [13] on the mean-field level. The model was developed further in different contexts [14–18] and recently reformulated in terms of the free energy functions for dissociable surface charges [7].

We base our analysis on the functional integral representation of the partition function generalized by the inclusion of a surface effective free energy that describes the

charge regulation. The model is solved exactly and the results provide insights into the correlations between the charge states of interacting surfaces. We go a step further and consider the interaction of two charged "particles" with a dielectric core and dissociable surface charge groups.

One dimensional electrolytes. – We consider a one dimensional system of positive and negative charges bounded by two charged interfaces located at $x = 0, L$. The charges interact with the unidimensional Coulomb interaction:

$$H = -\frac{1}{4} \sum_{ij} |x_i - x_j| q_i q_j = -\frac{1}{2} \sum_{ij} G_c(x_i, x_j) q_i q_j, \quad (1)$$

in units where the dielectric constant is unity. x_i is the position of the particle i carrying charge q_i and the Coulomb kernel $G_c(x, x')$ satisfies

$$\frac{\partial^2 G_c(x, x')}{\partial x^2} = -\delta(x - x'). \quad (2)$$

We can then use field theory mappings [2, 3], or analogies with a one-dimensional Brownian particle [5], to show that the free energy functional for an interacting symmetric one-one electrolyte is

$$S[\phi] = \int dx \left(\frac{1}{2} \beta \left(\frac{\partial \phi}{\partial x} \right)^2 - 2\lambda \cos(\beta e \phi) + i \rho_0 \phi \right) \quad (3)$$

where β is the inverse thermal energy, λ is the absolute activity of the electrolyte bath, e is the elementary charge, ρ_0 is an external fixed charge density and ϕ is a fluctuating potential which is integrated over to calculate the partition function (up to an irrelevant multiplicative constant)

$$Z = \int \mathcal{D}[\phi] e^{-S[\phi]}, \quad (4)$$

so $S[\phi]$ can be viewed appropriately as a field action. The prefactor of the functional integral is irrelevant for the specific context of this work.

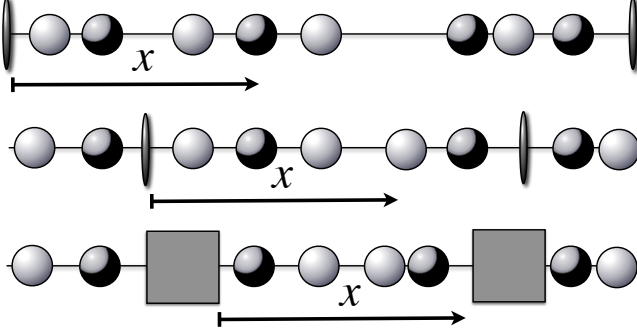


Figure 1: Schematic representation of the three considered systems. Top: two metallic interacting ionizable surfaces. Middle: two ionizable surfaces in an infinite electrolyte bath. Bottom: two dielectric "particles" with ionizable surfaces in an infinite electrolyte bath.

By rescaling the energy and the length scales in the problem we can work with an a -dimensional form of the interaction. We chose to scale the variables such that the bulk field action takes the form

$$S[\psi] = \frac{1}{2} \int_0^L dt \left(\frac{d\psi}{dt} \right)^2 - 2\bar{\lambda} \int_0^L dt \cos(\psi) \quad (5)$$

From now on we will use this form, measuring distances in units of the one-dimensional Bjerrum length $\ell_B = 1/e^2\beta$ and the fluctuating field action in thermal units. Note there is an inversion in the physics of one-dimensional electrolytes, compared to three dimensions. Particles interact weakly at small separations and strongly at the largest distances; the potential strength increasing with $|x_i - x_j|$. This implies that dense electrolytes, with large $\bar{\lambda}$ are described by the simpler weakly interacting theory. For small $\bar{\lambda}$ particles can form interacting, bound Bjerrum pairs [4].

The remarkable feature of the one dimensional partition function that we will exploit [4] is that the non-linear weighting eq. (4) maps onto another *linear* problem. This mapping is essentially the same as the mapping from the path-integral to the Schrödinger formulations of quantum mechanics. We will thus be concerned with linear partial differential equations of the form

$$\frac{\partial G_{\bar{\lambda}}(\psi, \psi'; t)}{\partial t} = \frac{1}{2} \frac{\partial^2 G_{\bar{\lambda}}(\psi, \psi'; t)}{\partial \psi^2} + 2\bar{\lambda} \cos(\psi) G_{\bar{\lambda}}(\psi, \psi'; t) \quad (6)$$

where the time like variable t is the position in the one-dimensional electrolyte measured in terms of the Bjerrum length and $G_{\bar{\lambda}}(\psi, \psi'; t)$ is a Green's function.

Surface free energy. – If external charges on the bounding surfaces $x = 0, L$ are considered to be equal and fixed at Ne , then they contribute

$$i\rho_0\phi \longrightarrow iNe\phi(0)\delta(x) + iNe\phi(L)\delta(x-L) \quad (7)$$

to the field action. However, we rather consider the case where each surface can be in a state of charge which varies from $-Ne$ to $(n_s - N)e$, corresponding to a surface charge group dissociation equilibrium. The chemical potential for dissociation is assumed to be independent of the number of previously bound ions, corresponding to the *charge regulation* paradigm [7]. On mapping to the field theory form we find that the surface free energy is given by the surface lattice gas expression:

$$e^{-\beta f(\psi)} = e^{-iN\psi + n_s \ln(1 + \lambda_S e^{i\psi})}. \quad (8)$$

where $\log \lambda_S$ is proportional to the free energy cost of charge dissociation. It will be useful to expand the logarithmic term into a *finite sum* to find

$$e^{-\beta f(\psi)} = e^{-iN\psi} (1 + \lambda_S e^{i\psi})^{n_s} \quad (9)$$

$$= \sum_{k=0}^{n_s} \binom{n_s}{k} \lambda_S^{n_s-k} e^{i(n_s-k-N)\psi}. \quad (10)$$

In our numerical applications we make the choice $n_s = 2N$ so that the surface can have a charge state which varies between $-Ne$ to $+Ne$, but other choices are possible.

The total partition function of two surfaces, separated by L in Bjerrum length units, interacting through a one-one electrolyte is then [5]

$$\Xi(L) = \int d\phi_0 \int d\phi_L e^{-\beta f(0)} G_{\bar{\lambda}}(\phi_0, \phi_L; L) e^{-\beta f(L)}. \quad (11)$$

This implies our principal result relating the partition function to a finite sum over Green functions:

$$\Xi(L) = \sum_{k,k'=0}^{n_s} \binom{n_s}{k} \binom{n_s}{k'} \lambda_S^{2n_s-k-k'} \times \int d\psi d\psi' e^{iM\psi} G_{\bar{\lambda}}(\psi, \psi'; L) e^{iM'\psi'} \quad (12)$$

with $M = n_s - N - k$, $M' = n_s - N - k'$. Let us consider the Fourier transformed Green function

$$\begin{aligned} Z_{M,M'}(L) &= \int d\psi d\psi' e^{iM\psi} G_{\bar{\lambda}}(\psi, \psi'; L) e^{iM'\psi'} \\ &= \int_0^{2\pi} d\psi e^{iM\psi} K(\psi, L). \end{aligned} \quad (13)$$

K can be expanded as a Fourier series

$$K(\psi, t) = \sum_{n=-\infty}^{\infty} b(n, t) e^{in\psi}. \quad (14)$$

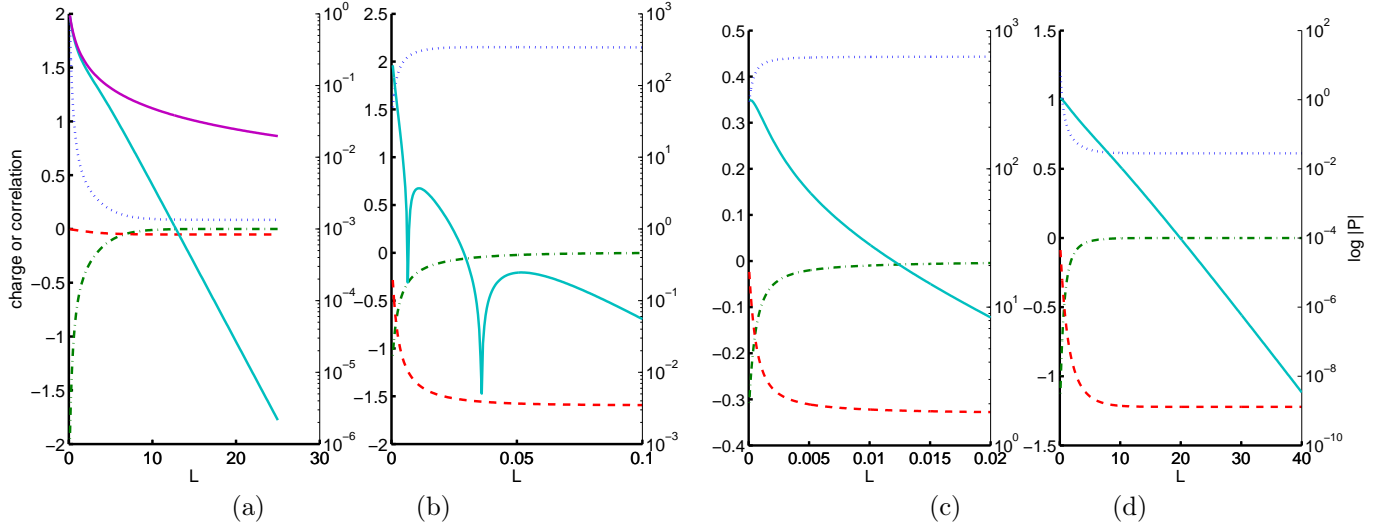


Figure 2: (a): Demonstration of the Kirkwood-Shumaker effect for two plates. Turquoise, solid line – Log of the disjoining pressure as a function of dimensionless separation (attractive interactions). Red dashed – average charge on a plate, blue dotted – mean square fluctuation of charge on a single plate, green dashed-dotted – charge correlation between two plates. $\bar{\lambda} = 0.02$ and $\lambda_S = 2$ with $N = 10$; top mauve line analytic expression eq. (22) valid for small separations. (b): Parameters for two plates demonstrating intermediate range attraction, but repulsion for small and large separations. $\lambda_S = 2$, $\bar{\lambda} = 10^3$, $N = 5$. This set of parameters leads to a minimum in the free energy at a finite separation between plates. (c): $N = 1$, $\lambda_S = 2$, $\bar{\lambda} = 10^3$. $N = 1$, plates are attracting. (d): $\bar{\lambda} = 0.1$ and $\lambda_S = 20$ with $N = 5$, $n_s = 10$, interaction is always repulsive.

$M \rightarrow M' = n_s - N - k'$, with the average defined as

$$\dot{b}_{nm}(t) = -\frac{1}{2}n^2 b_{nm}(t) + \bar{\lambda}(b_{n+1,m}(t) + b_{n-1,m}(t)). \quad (15)$$

The initial condition is that $b_{n,m}(0) = \delta_{n,-m}$. This is then a simple matrix equation $\dot{b} = \Gamma b$ with solution $b = e^{\Gamma t} \tilde{I}$, where \tilde{I} is a matrix that has unit elements on the *skew diagonal*, corresponding to complex conjugation. The matrix Γ has entries $-n^2/2$ on the diagonal and entries $\bar{\lambda}$ on the first step from the diagonal. The thermodynamics of the system is then deduced from

$$\Xi(L) = \sum_{k,k'=0}^{n_s} \binom{n_s}{k} \binom{n_s}{k'} \lambda_s^{2n_s-k-k'} b_{n_s-N-k, n_s-N-k'}(L), \quad (16)$$

where L is the extension of the system in the units of Bjerrum length. The disjoining pressure p , the average charge and its mean square fluctuations on the bounding surfaces, as well as the cross-correlation of the charge between the two surfaces can all be obtained straightforwardly from the above expression. The disjoining pressure in thermal units follows from the standard expression in the form

$$P = \frac{\partial}{\partial L} \log \Xi(L). \quad (17)$$

The mean surface charge $\langle M \rangle$ and the mean-square surface charge fluctuation $\langle M^2 \rangle$ are identical at both bounding surfaces, with $M = n_s - N - k$ at the boundary $x = 0$, or equivalently at the boundary $x = L$ with

$$\langle \dots \rangle = \frac{1}{\Xi} \sum_{k,k'=0}^{n_s} \binom{n_s}{k} \binom{n_s}{k'} \lambda_s^{2n_s-k-k'} (\dots) b_{M,M'}(L). \quad (18)$$

The cross-correlation function between charges on both surfaces, $\langle (M - \langle M \rangle) (M' - \langle M' \rangle) \rangle$, quantifies the correlation between the instantaneous charge at boundary $x = 0$ and boundary $x = L$ that depends on other parameters and the size of the system. The disjoining pressure is calculated within our code by the use of the relation

$$P = \langle \Gamma \rangle. \quad (19)$$

Interactions without electrolyte. – We first consider the case of two metallic plates. We impose strict electroneutrality on the system of plates so that the electric field is identically zero outside of the considered region [5] and start with the choice $\lambda_s = 1$, where the effects of monopole fluctuations can be expected to be strongest. The case involving $N = 1$ is particularly simple. There are three surface charge states possible: $(0, 0)$, $(e, -e)$, $(-e, e)$. The partition function is then $Z = 1 + 2e^{-\beta e^2 L/2}$ where we have used the energy $LE^2/2$ for the electric field with $E = q$ as the boundary condition. We find that the pressure

$$P = \frac{e^2}{(2 + e^{\beta e^2 L/2})} \quad (20)$$

looks rather like a Fermi function, having finite values at small separations and exponential decaying for separations

beyond the Bjerrum length. Charged states become exponentially rare at large separations since their energy increases with separation. This is a big difference with the three dimensional case where object can remain charged at large separations.

There is also an interesting and simple result for a large number of active sites ($N \gg 1$) in the limit $L < \ell_B$. We start with a simple argument neglecting discrete charges. The energy of a system with charge q on a single plate is $E = q^2 L/2$. Thus $Z = \int dq e^{-\beta q^2 L/2} \sim \frac{1}{\sqrt{L}}$. This gives the simple expression for the pressure

$$P \sim \frac{1}{2\beta} L^{-1} \quad (21)$$

While valid in the limit of very large N it gives a rather poor fit for moderate N . Much better results are obtained with the following modified argument which includes the entropy of the charge fluctuations. The propagation of modes within the electrolyte is given by eq. (15): $b(t) = e^{-n^2 t/2} \tilde{I}$. The surfaces are then described by a Gaussian approximation to the binomial coefficients for a near neutral surface with n the net number of charges: $\binom{2N}{N+n} \sim e^{-n^2/N}$. Then

$$Z = \int dn \left(e^{-n^2/N} \right)^2 e^{-n^2 L/2\ell_B} \sim \frac{1}{\sqrt{L/\ell_B + 4/N}}, \quad (22)$$

giving:

$$P = \frac{1}{2\beta} (L + 4\ell_B/N)^{-1}. \quad (23)$$

This fits very well the exact evaluation for $N > 10$ for $L < \ell_B$, see Fig (1a), even for $\lambda_s \neq 1$. Again for larger L there is an exponential decay in interactions.

Interactions within an electrolyte. – To evaluate our expressions within an electrolyte we work in a subspace corresponding to modes from $-n_m : n_m$ of dimension $2n_m + 1$. Using Matlab/Fortran labeling of the modes from 1 to $2n_m + 1$, the mode $m = 0$ has the position $i = n_m + 1$ in the matrix, and the mode m is at position $i_m = n_m + m + 1$. We can then evaluate all the expressions using matrix algebra. b is evaluated using the matrix exponential and the free energies are evaluated by grouping the combinatorial factors into right and left vectors.

We now consider the case of a low ion concentration, $\bar{\lambda} = 0.02$ and take the chemical potential for charging the plates as $\lambda_S = 2$. In figure (2 (a)) we plot the logarithm of the absolute value of the disjoining pressure as a function of the separation between the plates. We plot information on the charge state of the surface: The constraint of strict neutrality has strong influence on this behaviour. For separations larger than $\sim 5\ell_B$ the average charge of each plate (red dashed) is constant; however for small separations the average surface charge goes to zero. This we interpret as being due to the constraint of electro-neutrality imposed by the chosen boundary conditions: The system prefers to cancel the surface charge, rather than pulling in

counter-ions at small separations to ensure global electro-neutrality.

The fluctuations of the surface charge behave in a very different manner from the average: The mean squared charge on the surface (blue dotted) takes on a constant value for large separations, but **increases strongly** at smaller separations. Therefore, even though on average the plates are neutral they can at any moment be strongly charged. This is possible because there is a strong anti-correlation between the two plates demonstrated in the evolution of the green dashed-dotted curve – one surface obviously becomes positive and the other negative. Thus even though the average charge is driven to zero there is a strong monopole fluctuation which we should interpret as the Kirkwood-Shumaker effect [11,12]. The charge cross-correlation can be seen to decrease to zero at large separations due to the screening of electrostatic interaction by the electrolyte and the short range attraction in this configuration can be interpreted as being due to strong thermal monopole fluctuations.

Let us now consider a weakly coupled system with higher charge density $\bar{\lambda} = 10^3$. Rather rich behaviour is found as a function of the surface properties. For $\lambda_S = 2, N = 5$ we have two changes of sign of the disjoining pressure, figure (2 (a)), ¹ We find repulsion at both small and large separations, but a window of attraction at intermediate distances. There is also a somewhat different behaviour in the evolution of the charge state when compared to figure (2 (b)) – while the average charge is driven to zero as before, we see that the blue fluctuations also decrease at small separations so that monopole fluctuations are not strong enough to produce short distance attraction.

If we change the charge state of the surface so that $N = 1$ we find a much simpler purely attractive interaction between plates. Again the charge and fluctuations of the surface decrease at the smallest separations, figure (2 (c)). It is interesting to note that the amplitude of charge fluctuations remains high at all distances even if the correlation between the plates is only important at the smallest separations (when the sum of the blue and green curves is driven to zero by neutrality).

Finally we force the surface to charge more strongly by increasing the value of $\lambda_S = 20$, figure (2 (d)). In this case the average charge of the plates overwhelms the effects of fluctuations. Even for this case the plates eventually discharge (on average) at the smallest separation – but the charge state again fluctuates strongly.

We see from all of the figures in this section that the electro-neutrality constraint has a strong influence on the charge state, and charge correlations at small separations. The average charge is always driven to zero leaving strong monopolar fluctuations. In the next section we study a modified model in which the electro-neutrality condition

¹We plot pressures on logarithmic scales which gives characteristic singularities at sign changes.

between the plates is relaxed so that the surface can remain charged up to contact to see how this modifies the interaction.

Two charged surfaces in an infinite electrolyte bath. — In this section we consider that the charges are attached to a dielectric medium of zero thickness, with electrolyte on both sides of the charged sources. In this geometry we no longer force the average charge of each plate to zero at contact; we can expect this to increase the repulsion between the surfaces as a consequence.

The partition function, eq. (11), is now modified to

$$\Xi(L) = \lim_{D \rightarrow \infty} \int d\phi_0 d\phi_L G_{\bar{\lambda}}(0, \phi_0; D) e^{-\beta f(0)} G_{\bar{\lambda}}(\phi_0, \phi_L; L) e^{-\beta f(L)} G_{\bar{\lambda}}(\phi_L, 0; D), \quad (24)$$

where the electrolyte extends from $\lim_{D \rightarrow \infty} [-D, D]$ and we assumed that the potential at the boundaries of this interval vanishes.

In the low density regime figure (3 (a)) shows that while in this modified geometry the average charge on the plate does indeed fall slightly at small separations, it remains finite at contact. A similar curve calculated for larger concentration of the electrolyte shows that the charge state (both average and fluctuations) is only a weak function of the separation. However it is interesting to notice that the average charge is regulated by the chemical potentials of the free and bound charges. While the average charge on the surface is far from saturation, it resembles most clearly the standard boundary condition of constant surface charge, independent of separation between plates, for this set of parameters.

Finally we show that attraction is still possible, figure (3 (b)) even in this geometry, if the chemical potential of the surface is close to unity. In this case the average charge on the surface is small and again fluctuations can be an important component of the effective interaction. Note that the charge on each plate is strongly fluctuating, but the plates remain weakly correlated for all separations.

We next move on to consider a more sophisticated as well as a more realistic model specifically for protein interaction, which corresponds to a pair of interacting, dielectric particles with ionizable surface groups, that is embedded in an infinite electrolyte.

Two dielectric "particles" in an infinite electrolyte bath. — In this section we consider an idealization of a protein with ionizable amino acids on its surface represented in a one dimensional model. Each protein excludes the electrolyte and its interior core behaves as a simple dielectric "particle" with a dielectric constant different from its "bulk" value, allowing in principle for the inclusion of the polarization effects.

For simplicity we will take the dimension of this dielectric regions as constant and equal to the Bjerrum length. In general it depends on their actual thickness as well as on the dielectric discontinuity through the definition of the

Bjerrum length. The two surfaces of each dielectric region are then described by our charge-regulated model. We thus study a model of two pairs of charge-regulated surfaces, each of them with a dielectric core, which interact through an electrolyte solution. Apart from the obvious limitations of a one dimensional model, this is as close as we can get to the realistic description of the interactions between two proteins in an electrolyte solution.

The partition function in this case is analogous to eq. (24) but we need to substitute

$$\int d\phi_0 e^{-\beta f(0)} \rightarrow \iint d\phi_{-h} d\phi_h e^{-\beta f(-h)} G_0(\phi_{-h}, \phi_h; 2h) e^{-\beta f(h)} \quad (25)$$

and

$$\int d\phi_L e^{-\beta f(L)} \rightarrow \iint d\phi_{L-h} d\phi_{L+h} e^{-\beta f(L-h)} G_0(\phi_{L-h}, \phi_{L+h}; 2h) e^{-\beta f(L+h)} \quad (26)$$

where $G_0(\phi, \phi'; t)$ stands for the dielectric region without salt, i.e., $\bar{\lambda} = 0$, representing the "particles" of which one spans the interval $[-h, h]$ and the other one $[L-h, L+h]$. In our numerical studies $2h$ equals one Bjerrum length.

It is clear that a number of interesting quantities can evolve as a function of the separation of particles. As we have seen above, the total charge of the particle will evolve, but it is also clear that this will happen in an un-even manner for the charge facing the other particle or facing the bulk electrolyte. Thus there will also be a dipole moment for each particle, which will naturally be anti-correlated between the two particles and will increase in amplitude at small separations. This parallels very closely the original Kirkwood-Shumaker analysis [11,12] that also considers separately monopolar fluctuations of the protein charge, as well as the associated fluctuations of the protein dipolar moment of the surface charge distribution.

We firstly consider the interaction between two "particles" at low electrolyte concentration and therefore small screening, figure (3 (c)). In this region of the parameter space we find attraction at all separations between the particles, different from the previous case (figure 3 (a)), where the disjoining pressure was uniformly repulsive. The total charge and the dipole moment of the "particles" show pronounced evolution as a function of separation, with both in general decreasing in absolute value with the separation. The attraction is generated predominantly by the enhanced charge and dipolar moment correlations, originating from both "particles", while the average dipole moment of each "particle" is antisymmetric and contributes an additional repulsion.

The case of a denser electrolyte with small surface chemical potential is presented in figure (3 (d)). As is already to be expected from the simpler infinitely thin plate models,

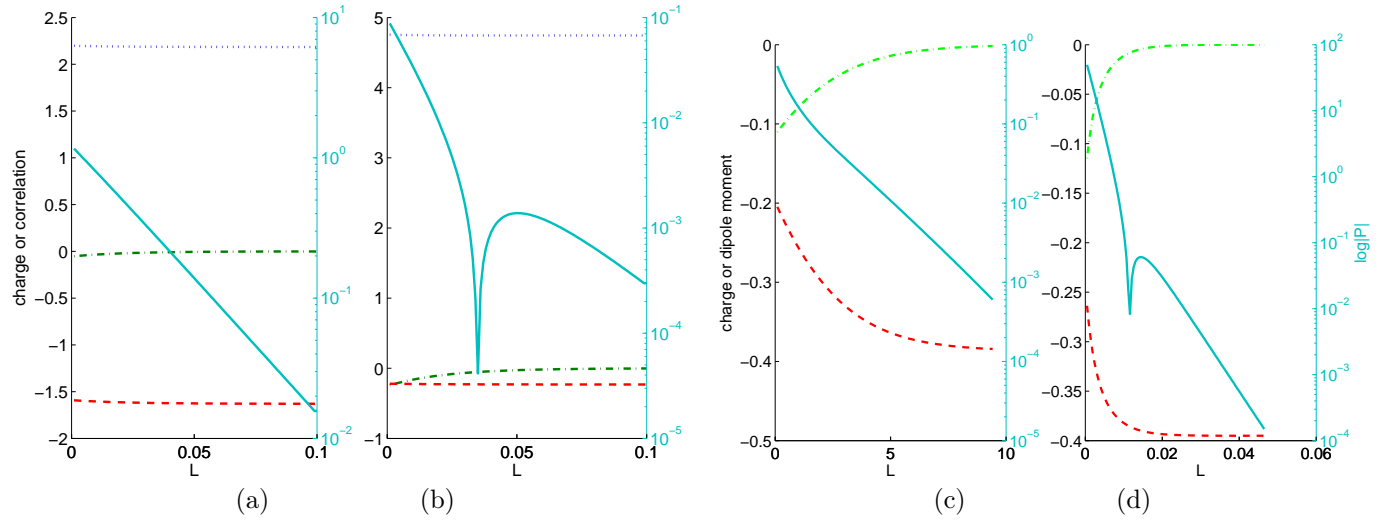


Figure 3: Same color and curve coding as in figure 2. Plates within electrolyte. (a): $\lambda_S = 2$, $\bar{\lambda} = 10^3$, $N = 5$. The disjoining pressure is uniformly repulsive, but the charge state of the surface is stable as a function of the separation. (b): The small value of $\lambda_S = 1.05$ only weakly charges the surface, but fluctuations remain very large. This leads to short range attraction between the surfaces. $N = 10$. (c): Disjoining pressure found to be attractive for all separations between charged dielectric "particles". The average charge (red dashed) and the dipole moment (green dashed-dotted) evolve as a function of the separation between the particles. $\bar{\lambda} = 10^{-1}$, $\lambda_S = 2$, $N = 5$. (d): Short range attractive, and long ranged repulsive interactions. The average charge (red dashed) evolves as a function of the separation as does the dipole moment of each particle (green dashed-dotted). $\bar{\lambda} = 10^3$, $\lambda_S = 1.1$, $N = 5$.

we generate interactions with short ranged attraction and longer ranged repulsion. Again we give the evolution of the charge and dipole states of the particles both showing pronounced dependence on the separation.

Conclusions. — We have demonstrated a rich variety of behaviours in a series of models incorporating ionizable charge-regulated surfaces, i.e., surfaces that respond to the local electrostatic potential with a variable effective charge, solved exactly in one dimension.

In the first model, of a pair of chargeable metallic plates, an important part of the physics comes from the possibility of driving the surface charge to zero at small separation. When this happens, large, correlated fluctuations occur which can lead to attractive interactions of a Kirkwood-Shumaker type.

A second model of two neutral plates in an infinite electrolyte bath considerably weakens the effect of global charge neutrality. But with chemical potentials close to unity, implying small charge dissociation energy penalty, fluctuation effects can still be very strong at the surfaces, affecting their interaction.

A third model is inspired directly by the work of Kirkwood-Shumaker on the effect of charge fluctuations and their role in the interactions between proteins, here idealised as dielectric "particles" of finite size with dissociable surface charge groups. This model takes into account the charge regulation of dissociable groups (amino acids) on the surface as well as the fluctuations of the mono polar and dipolar components of the fluctuating charge distribution, being thus closest to the original Kirkwood-

Shumaker proposition [11,12].

We expect that at least some of the properties of these models will transfer also to the more realistic 3D models of the interaction between globular proteins with dissociable surface charge groups. Our analysis suggests that there might be features of electrostatic interactions between macro ions bearing dissociable charged groups that have heretofore not been specifically considered in the models of protein-protein interaction [10].

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